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by

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Convenient Route to Di- and Triorganosilyl Ethyl Ethers and the Corresponding Di- and Triorganosilanes

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Abstract

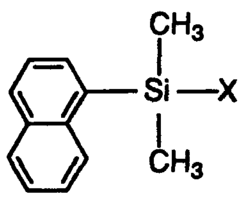
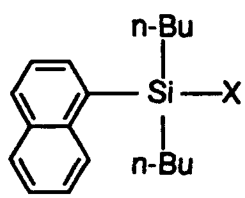
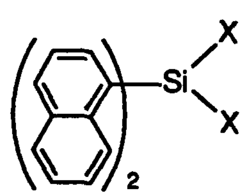
Tetraethoxysilane was treated with alkyl- and aryllithium reagents for the preparation of organosilyl ethyl ethers of the type R_3SiOEt, $R_2R'SiOEt$, and $R_2Si(OEt)_2$, that can be reduced to the organosilanes R_3SiH, $R_2R'SiH$, and R_2SiH_2, respectively. Compounds of the type RR'R"SiOEt can not be cleanly formed. The reduction procedure involves treatment of the silyl alkoxy ethers with diisobutylaluminum hydride (DIBALH) and hydrolysis of the remaining alkylaluminum compounds with $Na_2SO_4 \cdot 10H_2O$. This hydrolysis procedure provides a convenient method for the isolation of R_3SiH, $R_2R'SiH$, and R_2SiH_2 compounds without hydrolysis of the Si-H moiety that often occurs in standard aqueous work-up procedures of unhindered silanes.

Di- and triorganosilanes have become extremely important for the synthesis of various silicon-containing materials by the use of metal-catalyzed hydrosilylation methods.[2] We became interested in preparing a number of di- and trisubstituted silanes, some of which had to have mixed substitution patterns, for example $R_2R'SiH$. Early reports indicated that formation of R_3SiCl or R_2SiCl_2 compounds by the addition of organolithium or Grignard reagents to silicon tetrachloride was not selective due to the high reactivity of the chlorides.[3] There were some reports of reactions of organolithium reagents with tetraalkoxysilanes to give compounds of the type R_3SiOEt and R_4Si. Only one case of a mixed tetra(aryl)silane ($R_2R'_2Si$) was reported.[4] Conversion of triorganosilyl alkoxy ethers, R_3SiOR', to the correspond hydrido compounds or triorganosilanes, R_3SiH, has been reported using diisobutylaluminum hydride (DIBALH), however, the scope and limitations of this method and detailed experimental procedures were not disclosed.[5] More recently, the mechanism for the addition of nucleophiles, including hydride addition, to alkoxysilanes has been thoroughly investigated.[6]

Here we define the methods and limitations involved in the addition of alkyl- and aryllithium reagents to tetraethoxysilane. We also describe the procedures necessary for the reduction of the alkoxy moiety using DIBALH. This involves a method for the hydrolysis of excess DIBALH and alkylaluminum intermediates using $Na_2SO_4 \cdot 10H_2O$, a procedure that does not interfere with the Si-H linkage. This is especially important in unhindered triorganosilanes and diorganosilane products.

Table I indicates several alkoxysilanes that were formed by treating tetraethoxysilane with organolithium reagents. Both alkyl- and aryllithium reagents add well to displace the alkoxide groups and trialkyl-, triaryl-, or diarylsilyl ethyl ethers can be formed (entries 1,7,8, and 9). The corresponding Grignard reagents are far less effective for the substitution reactions.[7]

Table I. Conversion of $(CH_3CH_2O)_4Si$ to Organosilyl Ethyl Ethers ($X = OCH_2CH_3$) Using Organolithium Reagents and to the Corresponding Silanes ($X = H$) Using DIBALH.[a]

entry	silane products	% yield for $X = OCH_2CH_3$	% yield for $X = H$ [b]
1	$(n\text{-}C_4H_9)_3Si—X$	66	60 (99)
2	$Ph(CH_3)_2Si—X$	52	-- (65)
3	$(p\text{-}Br\text{-}C_6H_4)(CH_3)_2Si—X$	56	50 (73)
4[c]	$(p\text{-}H_3C\text{-}C_6H_4)—Si(s\text{-}Bu)_2—X$	44	50 (76)
5		44	42 (83)
6		46	70 (82)
7	$Ph_3Si—X$	51	69 (89)
8	$(p\text{-}H_3C\text{-}C_6H_4)_2SiX_2$	44	62 (85)
9		70	73

[a] See the experimental section for details. [b] Yields are isolated yields of material

obtained by distillation or crystallization. Yields in parentheses are GC yields determined using the response ratio of the product relative to an *n*-alkane internal standard.

Mixed trisubstituted ethers could also be formed by the addition of two equivalents of an organolithium reagent (RLi) followed by one equivalent of a second organolithium reagent (R'Li) (eq 1). The reverse mode of addition can not be used since monoalkyl- or monoaryl(triethoxy)silane is more prone to attack by an organolithium reagent than is tetraethoxysilane (eq 2). Hence, this prohibits the use

$$2\,RLi + Si(OEt)_4 \longrightarrow R_2Si(OEt)_2 \xrightarrow{R'Li} R_2R'SiOEt \qquad (1)$$

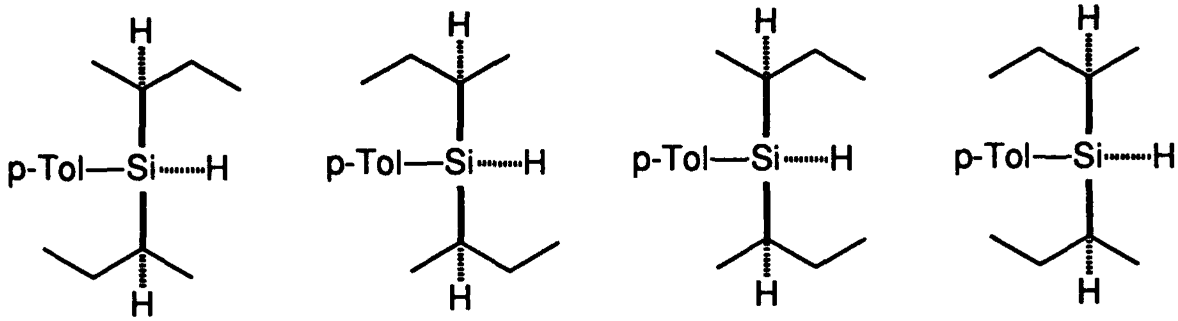
$$RLi + Si(OEt)_4 \longrightarrow 1/2\,R_2Si(OEt)_2 + 1/2 \text{ unreacted } Si(OEt)_4 \qquad (2)$$

R and R' = alkyl or aryl

of this approach for the clean formation of the mixed silyl ethyl ethers of the type $RR'Si(OEt)_2$ or RR'R"SiOEt.

Reduction of the alkoxysilanes to the corresponding hydrido species was easily achieved using DIBALH in toluene at room temperature. The reaction times were generally 0.5-2.5 h using 1.9-2.0 equivalents of DIBALH per ethoxysilane bond. Original reports of 5 min reaction times with one equivalent of reducing agent could not be obtained with our systems.[5] The reaction mixtures were quenched by adding Na_2SO_4-$10H_2O$ in order to hydrolyze excess hydride and alkylaluminum species. Upon cessation of bubbling, the slurry was filtered through a plug of silica gel, the solvent was removed and the silane distilled or crystallized directly. This procedure avoids the standard aqueous work-up necessary for the quenching of excess DIBALH and alkylaluminum species. Hence, especially sensitive unhindered trialkylsilanes and diorganosilanes could be obtained with limited hydrolysis of the Si-H moiety (Table 1, entries 1, 8, 9).

Interestingly, for entry 4, three isomers for both the ethoxy and hydrido compounds were observed by ^{13}C NMR. This is consistent with the formation of the enantiomeric pair **1** and **2**, and the two meso forms **3** and **4**, depicted using the



1 **2** **3** **4**

hydrido species.

In summary, a convenient approach to the di- and triorganosilylalkoxides has been described and the limitations of this approach for the preparation of unsymmetrical systems was outlined. Additionally, a method for the conversion of the alkoxides to the corresponding silanes was described using DIBALH and a modified hydrolysis procedure.

Experimental Section

General. All operations were carried out under a dry, oxygen-free, nitrogen atmosphere. Reagent grade diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade toluene was distilled under nitrogen from calcium hydride. Bulk grade hexane was distilled prior to use. Tetraethoxysilane was purchased from Aldrich Chemical Company, distilled over calcium hydride, and stored under nitrogen. *n*-Butyllithium, *sec*-butyllithium, and methyllithium were purchased from Aldrich Chemical Company and titrated prior to use by the method of Watson and Eastham.[8] *tert*-Butyllithium was purchased from Aldrich Chemical Company or Lithium Corporation of America and titrated prior to use.[8] Proton NMR spectra were recorded at 300 or 500 MHz on Brüker AM-300 or Brüker AM-500 spectrometers, respectively. The ^{13}C NMR spectra at 75 or 125 MHz were recorded on a Brüker AM-300 or Brüker AM-500 spectrometers, respectively. Proton chemical shifts (δ) are reported in ppm down field from tetramethylsilane (TMS) and ^{13}C resonances were recorded using the 77.0-ppm $CDCl_3$ resonance of the solvent as an internal reference and are reported in ppm down field from TMS. Infrared (IR) spectra were recorded on a Perkin Elmer 1600 Series FTIR. The accurate-mass spectra were determined on a VG Analytical, Ltd., 70SQ high resolution, double-focusing mass spectrometer equipped with a VG 11/250 data system. Combustion analyses were obtained from Atlantic Microlab, Inc., P.O. Box 2288, Norcross, GA 30091. Capillary GC analyses were obtained using a Hewlett Packard Model 5890 gas chromatograph using a Hewlett Packard 3396A integrator. Flash chromatography was carried out on 230-400 mesh silica gel purchased from EM Science. In all experimental procedures, flash chromatography refers to chromatography with a nitrogen head pressure as described by Still.[9] The GC yields were often greater than the isolated yields due to the difficulties in distilling or crystallizing the products on the small scales used. Larger scales should afford yields much closer to the GC values listed.

Ethoxy(tri-*n*-butyl)silane.[10] Tetraethoxysilane (1.1 mL, 0.00493 mole) in ether (5 mL) was cooled to -78°C. *n*-butyllithium (6.0 mL, 0.0149 mole, 2.48 M in hexane) was added and the reaction was allowed to warm to room temperature for 1 h. The reaction was quenched with water and the organic phase was dried over magnesium sulfate. The solvent was removed in vacuo, and the crude oily product was purified by flash chromatography (silica gel, hexane --> hexane/ether 20:1) to yield 0.80 g (66%) of the title compound as a clear colorless oil (95% GC purity). IR (neat) 2922.4, 1465.2, 1377.2, 1296.9, 1194.2, 1110.9, 1080.3, 944.9, 885.6, 762.5. ^1H NMR ($CDCl_3$, 500 MHz) δ 3.64 (q, J = 7.0 Hz, 2 H), 1.30 (m, 12 H), 1.16 (t, J = 7.0 Hz, 3 H), 0.87 (m, 6 H), 0.57 (m, 9 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 58.35, 26.62, 25.42, 18.65, 13.77, 13.36. HRMS calc'd for $C_{14}H_{32}SiO$: 244.2222. Found: 244.2220.

Dimethyl(ethoxy)(phenyl)silane.[11] Tetraethoxysilane (1.1 mL, 0.00493 mole) in ether (5 mL) was cooled to -78°C. Methyllithium (7.1 mL, 0.00994 mole, 1.4 M in ether) was added and the reaction was allowed to warm to room temperature for 30 min. Phenyllithium [prepared by adding bromobenzene (0.55 mL, 0.00522 mole) in ether (3 mL) to a solution of *t*-butyllithium (5.9 mL, 0.0100 mole, 1.7 M in pentane) in ether (2 mL) at -78°C and stirring for 1 h] was added at -78°C. After warming to room temperature for 1.5 h, the reaction was quenched with water (20 mL) and the organic phase was dried over magnesium sulfate. The solvent was removed in vacuo, and the crude oily product was distilled under vacuum (75°C, 0.8 mm Hg, Kugelrohr) to yield 0.46 g (52%) of the title compound as a clear colorless oil (93% GC purity). IR (neat) 2970.6, 1427.9, 1251.4, 1116.4, 947.7, 826.6, 785.9, 699.1. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.56 (m, 2 H), 7.35 (m, 3 H), 3.65 (q, J = 7.0 Hz, 2 H), 1.16 (t, J = 7.0 Hz, 3 H), 0.36 (s, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.02, 133.45, 129.52, 127.81, 58.67, 18.42. HRMS calc'd for $C_{10}H_{16}SiO$: 180.0970. Found: 180.0968.

4-Bromophenyl(dimethyl)(ethoxy)silane.[12] The title compound was prepared analogous to dimethyl(ethoxy)(phenyl)silane using tetraethoxysilane (11.2 mL, 0.0502 mole) in ether (50 mL), methyllithium (72.0 mL, 0.101 mole, 1.4 M in ether) and 4-bromophenyllithium [prepared by adding *t*-butyllithium (59 mL, 0.100 mole, 1.7 M in pentane) to a solution of 1,4-dibromobenzene (11.78 g, 0.0499 mole) in ether (30 mL) and THF (50 mL) at -78°C and stirred at -78°C for 1 h]. After workup, the crude, oily product was distilled under vacuum (70-80°C, 1.1mm Hg, Kugelrohr) to yield 7.23 g (56%) of the title compound as a clear colorless oil (94% GC purity). IR (neat) 2970.9, 1574.2, 1479.2, 1376.3, 1254.0, 1164.2, 1068.0, 1011.1, 948.8, 824.3, 783.4, 722.3. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.49 (1/2 ABq, J = 8.2 Hz, 2 H), 7.41 (1/2 ABq, J = 8.2 Hz, 2 H), 3.64 (q, J = 6.9 Hz, 2 H), 1.16 (t, J = 7.0 Hz, 3 H), 0.35 (s, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.87, 135.04, 130.99, 124.39, 58.72, 18.40, -1.77. HRMS cal'd for $C_{10}H_{15}Si^{79}BrO$: 258.0076. Found: 258.0079.

Di-*sec*-butyl(ethoxy)(4-methylphenyl)silane. The title compound was prepared in a manner analogous to the preparation of dimethyl(ethoxy)(phenyl)silane using tetraethoxysilane (2.2 mL, 0.00986 mole) in ether (10 mL), *sec*-butyllithium (18.6 mL, 0.0197 mole, 1.1 M in cyclohexane) and 1-lithio-4-methylbenzene [prepared by adding 4-bromotoluene (1.69 g, 0.00988 mole) in ether (5 mL) to a solution of *t*-butyllithium (8.6 mL, 0.0198 mole, 1.7 M in pentane) in ether (5 mL) at -78°C and stirring at -78°C for 1 h]. After workup, the crude, oily product was distilled under vacuum (120°C, 0.7 mm Hg, Kugelrohr) to yield 1.20 g (44%) of the title compound as a clear colorless oil (98% GC purity). IR (neat) 2959.2, 2870.6, 1604.4, 1459.7, 1390.3, 1160.2, 1107.0, 998.5, 945.3, 850.4, 799.8, 750.6, 699.9, 667.2. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.40 (d, J = 7.9 Hz, 2 H), 7.16 (d, J = 7.6 Hz, 2 H), 3.76 (q, J = 6.9 Hz, 2 H), 2.33 (s, 3 H), 1.69-1.60 (m, 2 H), 1.22 (t, J = 6.9 Hz, 3 H), 1.11-0.88 (m, 16 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.86, 134.65, 134.62, 134.59, 131.48, 131.40, 131.31, 128.40, 59.39, 59.36, 59.33, 24.19, 24.11, 21.51, 19.77, 19.62, 19.60, 18.62, 13.56, 13.44, 13.40, 13.27, 13.26, 13.09, 13.07. HRMS calc'd for $C_{17}H_{30}SiO$: 278.2066. Found: 278.2060.

Dimethyl(ethoxy)(1-naphthyl)silane. The title compound was prepared in a manner analogous to the preparation of dimethyl(ethoxy)(phenyl)silane using tetraethoxysilane (1.1 mL, 0.00493 mole) in ether (5 mL), methyllithium (7.1 mL, 0.00994 mole, 1.4 M in ether) and 1-naphthyllithium [prepared by adding 1-bromonaphthalene (0.70 mL, 0.00503 mole) in ether (2 mL) to a solution of *t*-butyllithium (5.9 mL, 0.0100 mole, 1.7 M in pentane) in ether (2 mL) at -78°C and stirring at -78°C for 1 h]. After workup, the crude, oily product was distilled under vacuum (115-125°C, 0.8 mm Hg, Kugelrohr) to yield 0.50 g (44%) of the title compound as a clear colorless oil (96% GC purity). IR (neat) 3055.8, 2970.8, 1589.5, 1505.6, 1390.5, 1320.1, 1252.7, 1077.9, 985.6, 946.4, 783.7, 672.4, 636.9. ^1H NMR ($CDCl_3$, 500 MHz) δ 8.32 (dd, J = 8.1, 0.9 Hz, 1 H), 7.87 (br d, J = 8.2 Hz, 1 H), 7.85 (dd, J = 7.8, 0.8 Hz, 1 H), 7.72 (dd, J = 6.8, 1.3 Hz, 1 H), 7.55-7.42 (m, 3 H), 3.67 (q, J = 7.0 Hz, 2 H), 1.18 (t, J = 7.0 Hz, 3 H), 0.54 (s, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.90, 135.96, 133.78, 133.29, 130.37, 128.83, 128.26, 125.95, 125.50, 124.97,58.73, 18.38, -0.52. HRMS calc'd for $C_{14}H_{18}SiO$: 230.1127. Found: 230.1127.

Di-*n*-butyl(ethoxy)(1-naphthyl)silane. The title compound was prepared analogously to dimethyl(ethoxy)(phenyl)silane using tetraethoxysilane (1.1 mL, 0.00493 mole) in ether (5 mL), *n*-butyllithium (3 9 mL, 0.00983 mole, 2.52 M in hexane) and 1-naphthyllithium [prepared by adding 1-bromonaphthalene (0.70 mL, 0.00503 mole) in ether (3 mL) to a solution of *t*-butyllithium (5.9 mL, 0.0100 mole, 1.7 M in pentane) in ether (2 mL) at -78°C and stirring at -78°C for 1 h]. After workup, the crude, oily product was distilled under vacuum (175-200°C, 0.8-1.4 mm Hg, Kugelrohr) to yield 0.71 g (46%) of the title compound as a clear colorless oil (97% GC purity). IR (neat) 2923.2, 1505.7, 1458.1, 1078.1, 944.9, 821.8, 777.4. ^1H NMR ($CDCl_3$, 500 MHz) δ 8.32 (dd, J = 7.8, 0.9 Hz, 1 H), 7.85 (br d, J = 8.2 Hz, 1 H), 7.83 (dd, J = 7.8, 1.8 Hz, 1 H), 7.70 (dd, J = 6.8, 1.3 Hz, 1 H), 7.55-7.41 (m, 3 H), 3.70 (q, J = 7.0 Hz, 2 H), 1.40-1.30 (m, 8 H), 1.21 (t, J = 7.0 Hz, 3 H), 1.08 (t, J = 7.8 Hz, 4 H), 0.90 (t, J = 7.2 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.27, 134.88, 134.24, 133.28, 130.16, 128.78, 128.30, 125.81, 125.41, 124.94, 58.82, 26.50, 25.39, 18.41, 14.21, 13.69. HRMS calc'd for $C_{20}H_{30}SiO$: 314.2066. Found: 314.2062.

Ethoxy(triphenyl)silane.[13] Ether (10 mL) was cooled to -78°C and *t*-butyllithium (18.0 mL, 0.0306 mole, 1.7 M in pentane) was added. A solution of bromobenzene (1.60 mL, 0.0152 mole) in ether (5 mL) was prepared and added to the *t*-butyllithium solution. After stirring for 1 h at -78°C the prepared phenyllithium was added to tetraethoxysilane (1.10 mL, 0.00493 mole) in ether (5 mL) at -78°C. The reaction mixture was allowed to warm to room temperature over 1 h. After quenching with water (30 mL), the organic phase was dried over magnesium sulfate. The solvent was removed in vacuo and the crude solid was purified by flash chromatography (silica gel, hexane/methylene chloride 15:1) to yield 0.76 g (51%) of the title compound as a white crystalline solid (98% GC purity). IR (KBr) 3066.9, 2968.2, 1588.8, 1428.8, 1390.1, 1117.8, 1079.6, 949.1, 638.9. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.62-7.60 (m, 6 H), 7.43-7.34 (m, 9 H), 3.86 (q, J = 7.0 Hz, 2 H), 1.22 (t, J = 7.0 Hz, 3 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.37, 134.43, 129.93, 127.82, 59.73, 18.37. HRMS calc'd for $C_{20}H_{20}SiO$: 304.1283. Found: 304.1281. Anal. Calc'd for $C_{20}H_{20}SiO$: C, 78.90; H, 6.62. Found: C, 78.40; H, 6.60.

Diethoxy(di-4-methylphenyl)silane.[14] *t*-Butyllithium (17.4 mL, 0.0400 mole, 2.3 M in pentane) was added to ether (10 mL) and cooled to -78°C. 4-Bromotoluene (3.42 g, 0.0200 mole) in ether (10 mL) was added. The mixture was stirred for 1h at -78°C and then added to tetraethoxysilane (2.2 mL, 0.00986 mole) in ether (10 mL) at -78°C. The reaction mixture was allowed to warm to room temperature for 2 h. After quenching with water (30 mL) the organic phase was dried over magnesium sulfate and the solvent was removed in vacuo. The crude oily product was distilled under vacuum (150-175°C, 0.8mm Hg, Kugelrohr) to yield 1.30 g (44%) of the title compound as a clear colorless oil. IR (neat) 2973.3, 2923.8, 1602.5, 1391.6, 1165.2, 1077.6, 955.3, 802.4, 781.6, 728.6, 653.9. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.53 (d, J = 7.9 Hz, 4 H), 7.16 (d, J = 7.4 Hz, 4 H), 3.84 (q, J = 7.0 Hz, 4 H), 2.33 (s, 6 H), 1.22 (t, J = 7.0 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.97, 134.89, 129.79, 128.57, 58.76, 21.55, 18.30. HRMS calc'd for $C_{18}H_{24}SiO_2$: 300.1546. Found: 300.1545.

Diethoxy(di-1-naphthyl)silane.[4b] The title compound was prepared analogous to diethoxy(di-4-methylphenyl)silane using *t*-butyllithium (17.5 mL, 0.0403 mole, 2.3 M in pentane) in ether (10 mL), 1-bromonaphthalene (4.10 g, 0.0198 mole) in ether (10 mL), and tetraethoxysilane (2.2 mL, 0.00986) in ether (10 mL).

After workup, the crude product was recrystallized from hexane to yield 2.55 g (70%) of the title compound as white crystals. IR (KBr) 2970.0, 1504.9, 1388.9, 1218.0, 1074.8, 987.7, 829.0, 778.2, 738.8, 675.6, 552.6, 474.6. ^1H NMR ($CDCl_3$, 500 MHz) δ 8.31 (dd, J = 8.4, 0.7 Hz, 2 H), 8.10 (dd, J = 6.8, 1.3 Hz, 2 H), 7.90 (br d, J = 8.2 Hz, 2 H), 7.80 (dd, J = 8.6, 1.3 Hz, 2 H), 7.48 (dd, J = 8.2, 6.8 Hz, 2 H), 7.39 (m, 4 H), 3.83 (q, J = 7.0 Hz, 4 H), 1.23 (t, J = 7.0 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.07, 136.15, 133.23, 131.82, 130.93, 128.62, 128.44, 126.04, 125.44, 125.14, 59.14, 18.31. HRMS calc'd for $C_{24}H_{24}SiO_2$: 372.1546. Found: 372.1547. Anal. Calc'd for $C_{24}H_{24}SiO_2$: C, 77.38; H, 6.49. Found: C, 77.37; H, 6.46.

Tri-*n*-butylsilane.[15] Ethoxy(tri-*n*-butyl)silane (0.53 g, 0.00217 mole) and hexadecane (0.15 mL, 0.000512 mole as an internal standard) were added to toluene (3 mL). The solution was cooled to -78°C and DIBALH (0.75 mL, 0.00421 mole) was added. After stirring for 30 min at -78°C, the reaction mixture was allowed to warm to room temperature for 30 min. The reaction was complete by GC. Sodium sulfate decahydrate was added and the mixture was stirred until the gas evolution had stopped. The salts were removed by filtration through a silica plug. After the solvent was removed in vacuo, the crude product was distilled under vacuum (100°C, 0.8mm Hg, Kugelrohr) to yield 0.26 g (60%, GC yield 99%) of the title compound as a clear colorless oil (96% GC purity). IR (neat) 2918.3, 2099.9, 1464.0, 1410.5, 1377.2, 1295.9, 1192.2, 1081.9, 963.1, 892.8, 808.0. ^1H NMR ($CDCl_3$, 300 MHz) δ 3.64 (sept, J = 3.2 H, 1 H), 1.35-1.26 (m, 12 H), 0.87 (t, J = 6.9 Hz, 9 H), 0.59-0.53 (m, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 26.97, 26.38, 13.80, 11.06.

Dimethyl(phenyl)silane.[16] The title compound was prepared in a manner analogous to tri-*n*-butylsilane using dimethyl(ethoxy)(phenyl)silane (0.30 g, 0.00166 mole) and tetradecane (0.11 mL, 0.000423 mole as an internal standard) in toluene (3 mL) and DIBALH (0.60 mL, 0.00337 mole). After workup, the crude product was distilled under vacuum (30 mm Hg). However, the product could not be completely separated from toluene. Therefore the identity was established by GC coinjection of commercially available (Aldrich) phenyl(dimethyl)silane with the product of the reaction. The GC yield was 65% (100% GC purity). IR (neat) 2959.4, 2924.9, 2120.2, 1635.7, 1427.8, 1259.9, 1115.8, 879.8, 804.4, 709.0, 668.1. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55-7.51 (m, 2 H), 7.37-7.33 (m, 3 H), 4.41 (sept, J = 3.8 Hz, 1 H), 0.33 (d, J = 3.8 Hz, 6 H).

4-Bromophenyl(dimethyl)silane.[17] The title compound was prepared in a manner analogous to tri-*n*-butylsilane using 4-bromophenyl(dimethyl)(ethoxy)silane (1.30 g, 0.00502 mole) in toluene (5 mL) and DIBALH (2.70 mL, 0.0152 mole). After workup, the crude product was distilled under vacuum (80°C, 0.7-0.9 mm Hg, Kugelrohr) to yield 0.54 g (50 %) of the title compound as a clear colorless oil (99% GC purity). To determine the GC yield, another reaction was run using 4-bromophenyl(dimethyl)(ethoxy)silane (0.42 g, 0.00162 mole) and hexadecane (0.15 mL, 0.000512 mole as an internal standard) in toluene (3 mL) and DIBALH (0.55 mL, 0.00309 mole). The GC yield was 73%. IR (neat) 2959.6, 2122.8, 1575.4, 1478.8, 1378.2, 1251.0, 1067.2, 1012.0, 878.2, 836.4, 809.6, 764.5, 722.2. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.47 (1/2 ABq, J = 8.3 Hz, 2 H), 7.37 (1/2 ABq, J = 8.3 Hz, 2 H), 4.37 (sept, J = 3.7 Hz, 1 H), 0.31 (d, J = 3.7 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.19, 135.56, 130.99, 123.99, -3.87. HRMS calc'd for $C_8H_{10}Si^{79}Br$ $(M-H)^+$: 212.9735. Found: 212.9736.

Di-*sec*-butyl(4-methylphenyl)silane. The title compound was prepared in a manner analogous to *tri-n*-butylsilane using di-sec-butyl(ethoxy)(4-methylphenyl)silane (0.40 g, 0.00144 mole) and nonane (0.070 mL, 0.000392 mole as an internal standard) in toluene (3 mL) and DIBALH (0.50 mL, 0.00281 mole). After workup, the crude product was distilled under vacuum (150°C, 1.3 mm Hg, Kugelrohr) to yield 0.17 g (50%, GC yield 76%) of the title compound as a clear colorless oil. IR (neat) 2954.2, 2103.0, 1603.5, 1459.9, 1378.4, 1311.5, 1212.0, 1106.8, 1033.7, 1001.0, 792.1, 692.9, 636.1. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.48 (d, J = 7.9 Hz, 2 H), 7.14 (d, J = 7.6 Hz, 2 H), 3.99 (m, 1 H), 2.33 (s, 3 H), 1.53 (m, 1 H), 1.22 (m, 1 H), 1.03 (m, 4 H), 0.949 (d, J = 7.3 Hz, 3 H), 0.944 (d, J = 7.3 Hz, 3 H), 0.876 (t, J = 7.5 Hz, 3 H), 0.868 (t, J = 7.5 Hz, 3 H). ^{13}C NMR

($CDCl_3$, 125 MHz) δ 138.79, 135.65, 135.57, 135.50, 130.89, 130.65, 130.46, 128.50, 25.95, 25.81, 25.62, 25.60, 21.49, 18.26, 18.18, 18.04, 14.90, 14.78, 14.75, 13.22, 13.20, 13.16.

Dimethyl(1-naphthyl)silane.[18] The title compound was prepared in a manner analogous to tri-*n*-butylsilane using dimethyl(ethoxy)(1-naphthyl)silane (0.35 g, 0.00151 mole) and nonane (0.070 mL, 0.000392 mole as an internal standard) in toluene (3 mL) and DIBALH (0.50 mL, 0.00281 mole). After workup, the crude product was distilled under vacuum (110-120°C, 1.0 mm Hg, Kugelrohr) to yield 0.12 g (42%, GC yield 83%) of the title compound as a clear colorless oil (97% GC purity). IR (neat) 3054.7, 2958.9, 2120.0, 1505.2, 1250.5, 1144.1, 985.2, 882.3, 839.2, 779.2, 737.9, 644.9. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.11 (dd, J = 8.2, 0.8 Hz, 1 H), 7.87 (d, J = 8.2 Hz, 1 H), 7.85 (dd, J = 7.2, 1.7 Hz, 1 H), 7.72 (dd, J = 7.0, 1.3 Hz, 1 H), 7.45 (m, 3 H), 4.84 (sept, J = 3.7 Hz, 1 H), 0.48 (d, J = 3.8 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 136.93, 135.62, 133.61, 133.18, 129.98, 128.94, 127.59, 125.91, 125.52, 125.16, -3.26. HRMS calc'd for $C_{12}H_{14}Si$: 186.0865. Found: 186.0855. Anal. Calc'd for $C_{12}H_{14}Si$: C, 77.35; H,7.57. Found: C, 76.53; H, 7.34.

Di-*n*-butyl(1-naphthyl)silane. The title compound was prepared in a manner analogous to tri-*n*-butylsilane using di-*n*-butyl(ethoxy)(1-naphthyl)silane (0.47 g, 0.00149 mole) in toluene (2 mL) and DIBALH (0.80 mL, 0.00449 mole). After workup, the crude product was distilled under vacuum (185°C, 0.7-1.0 mm Hg, Kugelrohr) to yield 0.28 g (70%) of the title compound as a clear colorless oil (98% GC purity). To determine the GC yield, another reaction was run using di-*n*-butyl(ethoxy)(1-naphthyl)silane (0.42 g, 0.00134 mole) and tetradecane (0.10 mL, 0.000385 mole as an internal standard) in toluene (3 mL) and DIBALH (0.45 mL, 0.00252 mole). The GC yield was 82%. IR (neat) 3055.4, 2921.3, 2111.4, 1588.5, 1505.4, 1463.7, 1409.4, 1376.7, 1217.8, 1190.2, 1144.0, 1081.4, 1023.5, 983.1, 892.1, 793.1, 733.2. ^1H NMR ($CDCl_3$, 500 MHz) δ 8.09 (dd, J = 7.2, 1.7 Hz, 1 H), 7.85 (d, J = 7.6 Hz, 1 H), 7.83 (dd, J = 6.7, 1.9 Hz, 1 H), 7.70 (dd, J = 6.7, 1.3 Hz, 1 H), 7.45 (m, 3 H), 4.67 (p, J = 3.6 Hz, 1 H), 1.41-1.29 (m, 8 H), 1.02-0.96 (m, 4 *H*), 0.88 (t, J = 7.1 Hz, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ

137.32, 134.55, 134.48, 133.24, 129.83, 128.91, 127.80, 125.80, 125.46, 125.11, 27.11, 26.22, 13.73, 12.22. HRMS calc'd for $C_{18}H_{26}Si$: 270.1804. Found: 270.1802.

Triphenylsilane.[19] The title compound was prepared in a manner analogous to tri-*n*-butylsilane using ethoxy(triphenyl)silane (0.46 g, 0.00151 mole) and nonane (0.070 mL, 0.000392 mole as an internal standard) in toluene (3 mL) and DIBALH (0.50 mL, 0.00281 mole). After workup, the crude product was distilled under vacuum (170°C, 1.0 mm Hg, Kugelrohr) to yield 0.27 g (69%, GC yield 89%) of the title compound as a clear colorless oil (99% GC purity). IR (neat) 3067.8, 3010.6, 2123.5, 1588.0, 1485.8, 1428.2, 1328.5, 1186.7, 1114.3, 998.1, 804.0, 729.1, 696.8. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.58-7.55 (m, 6 H), 7.43-7.33 (m, 9 H), 5.45 (s, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 135.80, 133.32, 129.80, 128.04. HRMS calc'd for $C_{18}H_{16}Si$: 260.1022. Found: 260.1017.

Di-4-methylphenylsilane.[20] The title compound was prepared in a manner analogous to tri-*n*-butylsilane using diethoxy(di-4-methylphenyl)silane (0.64 g, 0.00213 mole) and decane (0.15 mL, 0.000770 mole as an internal standard) in toluene (3 mL) and DIBALH (1.45 mL, 0.00814 mole). After workup, the crude product was distilled under vacuum (135°C, 0.8 mm Hg, Kugelrohr) to yield 0.28 g (62%, GC yield 85%) of the title compound as a clear colorless oil (99% GC purity). IR (neat) 3012.8, 2920.5, 2134.2, 1601.4, 1391.9, 1114.1, 937.9, 850.3, 794.4, 628.8. ^1H NMR ($CDCl_3$, 500 MHz) δ 7.47 (d, J = 7.9 Hz, 4 H), 7.17 (d, J = 7.9 Hz, 4 H), 4.87 (s, 2 H), 2.34 (s, 6 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 139.77, 135.68, 128.93, 128.03, 21.51. HRMS calc'd for $C_{14}H_{16}Si$: 212.1022. Found: 212.1015.

Di-1-naphthylsilane.[21] The title compound was prepared in a manner analogous to tri-*n*-butylsilane using diethoxy(di-1-naphthyl)silane (1.12 g, 0.00301 mole) and tetradecane (0.25 mL, 0.000961 mole as an internal standard) in toluene (4 mL) and DIBALH (1.90 mL, 0.0107 mole). After workup, the crude product was recrystallized from hexane to yield 0.31 g (72%) of the title compound as a white crystalline solid. IR (KBr) 3047.5, 2159.7, 2133.8, 1503.6, 1327.8, 1217.5, 1141.0, 1021.8, 988.5, 938.8, 847.0, 782.8, 640.7, 597.0, 522.9, 508.8, 489.2. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.10 (br d, J = 8.7 Hz, 2 H), 7.93 (br d, J = 8.2 Hz, 2 H), 7.87 (dd, J = 7.3, 1.8 Hz, 2 H), 7.76 (d, J = 6.7 Hz, 2 H), 7.48 (m, 4 H), 7.43 (br t, J = 7.5 Hz, 2 H), 5.69 (s, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.38, 136.48, 133.14, 130.89, 129.65, 128.84, 127.89, 126.37, 125.84, 125.38. Anal. Calc'd for $C_{20}H_{16}Si$: C, 84.45; H, 5.67. Found: C, 83.45; H, 5.82.

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